SYNOPSIS

Application of III-V semiconductor alloys in optoelectronics is ever increasing due to their excellent electrical and optical properties compared to elemental silicon There has been growing interest in the determination of the thermodynamic properties and phase equilibria in the systems containing III-V elements for their superior properties The ability of the compounds in these systems to form substitutional solid solutions and the increased degree of property freedom in the multicomponent solid solutions provide the solid state device designer with a virtually continuous spectrum of properties to make the devices pertaining to the various applications The purpose of the present investigation is to develop thermodynamic insights into the Al-Ga, Al-In-Sb and Al-Ga-In-Sb systems based on experiments and thermodynamic modelling

The present research was undertaken to determine the thermodynamic properties and reassess the phase equilibria in the Al-Ga binary system The activities of Al in the liquid alloys have been determined by E M F technique using a concentrated cell of the type

$$W,Al(l)|NaCl + KCl + 3mole\ \%AlCl_3|Al_xGa_{(1-x)}(l),\ W$$

The measurements are carried out over a wide temperature range from 925 to 1275 K and a compositional range $x_{Ga} = 0.1$ to 0.9 The E M F data generated for the system exhibits linear relationship with temperature The activities of Al in the Al Ga alloys exhibit positive deviation from ideality The deviation is found to decrease progressively with increase in temperature and Al content of the alloys The calculated enthalpy of mixing of Al in the alloys is found to be asymmetric with respect to the composition and they are compared with those of the available in the literature The phase equilibria in the system are evaluated using the following five parameter excess free energy function based on the experimental data

$$\Delta G^{xs} = x(1-x)\left[a_1 + a_2T + a_3x + a_4x(1-x) + a_5x^2(1-x)\right]$$

where a_1 to a_5 are binary constants and 'x' is the molefraction of Al The calculated

solidus and the liquidus boundaries of the system based on the present investigation are in good agreement with those determined by the earlier evaluations and experimentally determined values available in the literature

In the Al-In-Sb ternary system, thermodynamic data have been generated using a E M F technique Although several investigations on the AlSb-InSb pseudo binary phase diagram and the enthalpy of mixing of the liquid Al-In-Sb alloys have been reported, the activity measurements of Al in this system are not available in the literature The E M F data have been generated using the concentrated cell of the type

$$W,Al(l) \mid NaCl + KCl + 3mol\ \%AlCl_3 \mid (Al+In+Sb)(l),W$$

The measurements are carried out along the constant compositional paths of x_{Sb} = 0 1 and 0 2 over a temperature range of 1073 to 1273 K The measured activity data in the system exhibit positive deviation from ideality The deviations increase progressively with the In content of the alloys for a constant compositional path of Sb The magnitude of the a_{Al} as a function of In is found to decrease significantly with the increase in the Sb content of the alloys The high positive deviation from ideality indicates the repulsive interaction between atoms which is consistent with the presence of miscibility gap in the system The partial molar enthalpies of mixing of Al in the system have been calculated based on the second law evaluation and have been found to decrease progressively with the Al and Sb contents of the alloys The experimental results have been analysed using a fifteen parameter integral excess free energy function as given below

$$\begin{aligned}\frac{\Delta G^{xs}}{RT} = {} & x_1x_2\{a_1x_1 + a_2x_2 + r_1x_2(a_3r_1 + a_4x_2)\} \\ & + x_1x_3\{a_5x_1 + a_6x_3 + r_1r_3(a_7x_1 + a_8r_3)\} \\ & + x_2x_3\{a_9x_2 + a_{10}r_3 + x_2x_3(a_{11}r_2 + a_{12}r_3)\} \\ & + x_1x_2x_3(a_{13}x_1 + a_{14}r_2 + a_{15}r_3)\end{aligned}$$

where a_1 to a_{12} are binary constants, and a_{13} to a_{15} correspond to ternary constants x_1, x_2, and x_3 refer to the molefractions of Al, In, and Sb respectively The liquid-liquid immiscibility gap in the system has been analysed using the experimental data based on the stability function as proposed by Lupis The calculated critical

composition for the onset of immiscibility, the composition pertaining to the liquid-liquid immiscibility gap compare favourably with those of the experimental data of the system reported in the literature The solid-liquid equilibria has been analysed using the experimental data generated in the system in the temperature range 1073 to 1173 K The calculated liquidus isotherms at 1073, 1123 and 1173 K are found to be in good agreement with those of the experimental data available in the literature

In the absence of any activity data for Al in the Al-Ga-In-Sb quaternary system, the present investigation is focused to generate the E M F data using a concentration cell of similar type as indicated earlier

$$\text{W, Al(l) | NaCl + KCl + 3 mole \% } AlCl_3 \text{ | Al-Ga-In-Sb(l), W}$$

The measurements are carried out on the liquid alloys along the constant compositional path of $\frac{x_{Ga}}{x_{In}} = 1$ with the Sb contents ranging from $x_{Sb} = 0.1$ to 0.3 over a temperature range of 1073 to 1273 K The activities of Al in the liquid alloys have been calculated using the E M F data generated in the present investigation which exhibit positive deviation from ideality along the constant compositional path $\frac{x_{Ga}}{x_{In}} = 1$ for a given Sb content of the alloys The deviation from ideality is found to decrease progressively with the Al content of the alloys The partial molar enthalpies of mixing of Al in the system calculated based on second law evaluation decreases progressively with increase in the Al and Sb content of the alloys The experimental data have been analysed using a thirty seven parameter excess free energy function is given below

$$\begin{aligned}
\frac{\Delta G^{ex}}{RT} = {} & r_1 r_2\{a_1 r_1 + a_2 r_2 + r_1 r_2(a_3 r_1 + a_4 r_2)\} \\
& + r_1 r_3\{a_5 r_1 + a_6 r_3 + r_1 r_3(a_7 r_1 + a_8 r_3)\} \\
& + r_1 r_4\{a_9 r_1 + a_{10} r_4 + r_1 r_4(a_{11} r_1 + a_{12} r_4)\} \\
& + r_2 r_3\{a_{13} r_2 + a_{14} r_3 + r_2 r_3(a_{15} r_2 + a_{16} r_3)\} \\
& + r_2 r_4\{a_{17} r_2 + a_{18} r_4 + r_2 r_4(a_{19} r_2 + a_{20} r_4)\} \\
& + r_3 r_4\{a_{21} r_3 + a_{22} r_4 + r_3 r_4(a_{23} r_3 + a_{24} r_4)\} \\
& + r_1 r_2 r_3\{b_1 r_1 + b_2 r_2 + b_3 r_3\} + r_1 r_2 r_4\{b_4 r_1 + b_5 r_2 + b_6 r_4\} \\
& + r_1 r_3 r_4\{b_7 r_1 + b_8 r_3 + b_9 r_4\} + r_2 r_3 r_4\{b_{10} r_2 + b_{11} r_3 + b_{12} r_4\} \\
& + r_1 r_2 r_3 r_4\{c\}
\end{aligned}$$

where a_1 to a_{12} are binary constants, b_1 to b_{12} are ternary constants, and 'c' is the quaternary constants. The molefractions x_1, x_2, x_3 and x_4 refer to Al, Ga, In, and Sb respectively. The derived partial based on the integral function of the quaternary system is capable of interpreting the experimentally determined activity coefficients for 1123 and 1173 K.

To represent the thermodynamic properties of dilute quaternary systems, Maclaurin infinite series has been used to express the integral excess free energy. The series is subjected to appropriate boundary conditions and each of the derivatives is correlated to corresponding interaction coefficients. The derivation of the partial functions involves extensive summation of the various infinite series pertaining to the first order and quaternary parameters to remove any truncational errors. The thermodynamic consistency has been established based on the Gibbs-Duhem relations. The applicability of the partials has been used to analyse the thermodynamic behaviour of nitrogen in the Fe-Cr-Ni-N and Fe-Ni-Ta-N quaternary systems. The calculated activity coefficients of nitrogen are in good agreement with those of the experimental data reported in the literature.